Advanced Oxidation & Stabilization of PAN-Based Carbon Precursor Fibers

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Status as of early March 2013

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Project ID: LM006

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY

MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Project Overview

Timeline

Phase **I**
- Start 2004
- End 2011

Phase **I** completed

Phase **II**
- Start 2011
- End 2015-16

Budget

- FY2011 $1,900,000 New
- FY2012 $1,000,000 New +$434,910 reprogrammed from other sources
- FY2013 $1,000,000 initially budgeted. $550,000 Received so far.

Barriers

- Barriers addressed
  - High cost of carbon fiber
  - Inadequate supply base for low cost carbon fibers/high volume production
  - Long conventional processing times for oxidative stabilization are the bottleneck in production

Partners

- ORNL (Host site), carbon fiber expertise, characterization
- ReMaxCo Technologies (Experimental site), atmospheric plasma and hardware development.

Collaborators

- At this moment none.

Presentation Outline

Project Objectives

Background

Approach

Milestones

Technical Accomplishments

Future Work

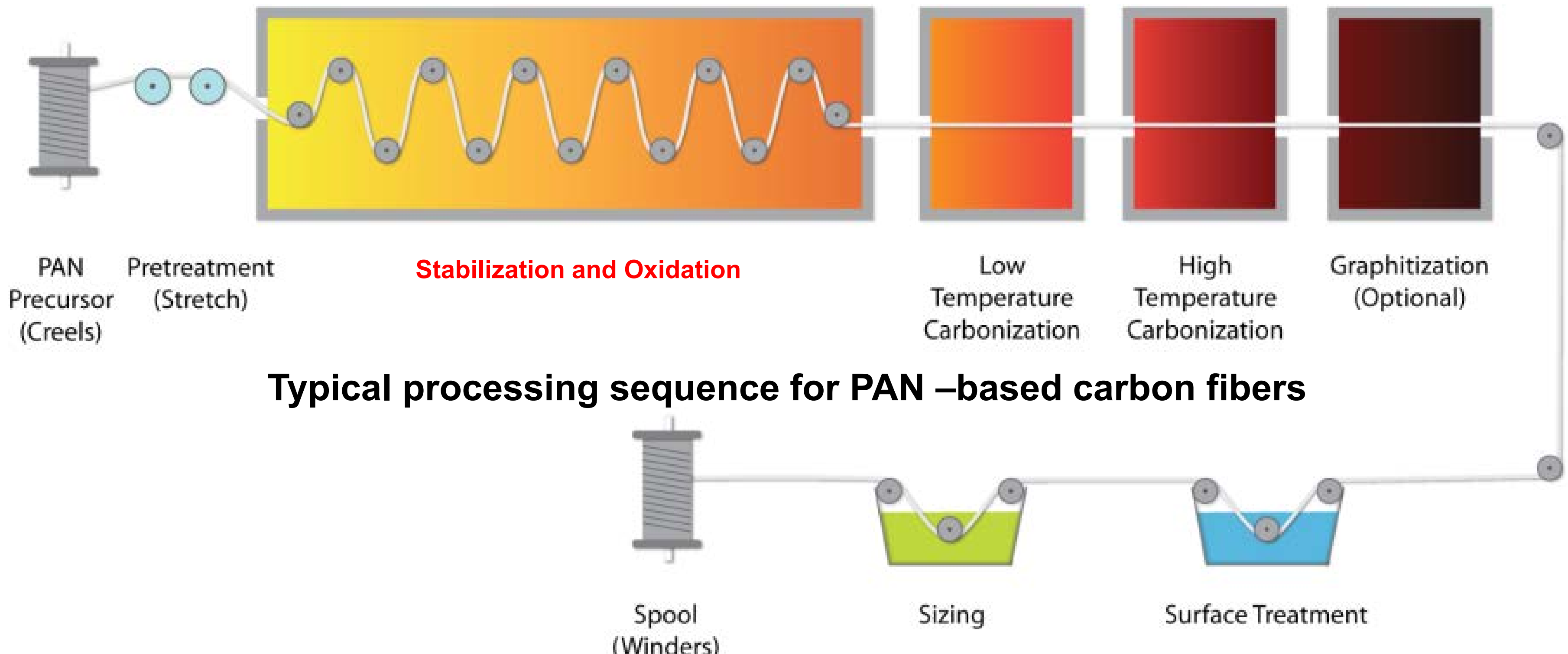
Conclusions

Project Objectives

- **Phase I: Produce up to three tows of carbon fiber meeting minimum program specifications (250 ksi tensile strength, 25 Msi Modulus, 1% strain) using oxidation residence time of 40 minutes or less.**
    - Oxidative stabilization is the bottleneck in the production process often requiring 90 to 120 minutes. By developing a 2-3X faster oxidation process, higher throughput and significant cost reduction can be achieved.
    - This phase is Complete.
- **Phase II: Demonstrate Phase I capability at Pilot Scale.**
    - This will involve up to six tows and up to 24k filament tows at less than 35 min residence time (increased throughput).
    - The Large Reactor used during this phase will have an estimated nameplate capacity of 1 ton/year.
    - This phase is In Progress.

Background

Conventional PAN Processing



Typical processing sequence for PAN –based carbon fibers

Major Cost Elements (Industrial Grade)

Precursor	51%	$5.04
Oxidative stabilization	16%	$1.54
Carbonization	23%	$2.32
Surface Treatment	4%	$0.37
Other (Spooling/Packaging)	6%	$0.62
Total		$9.88

Kline & Co Cost Model/2007

Automotive cost target is $5 - $7/lb

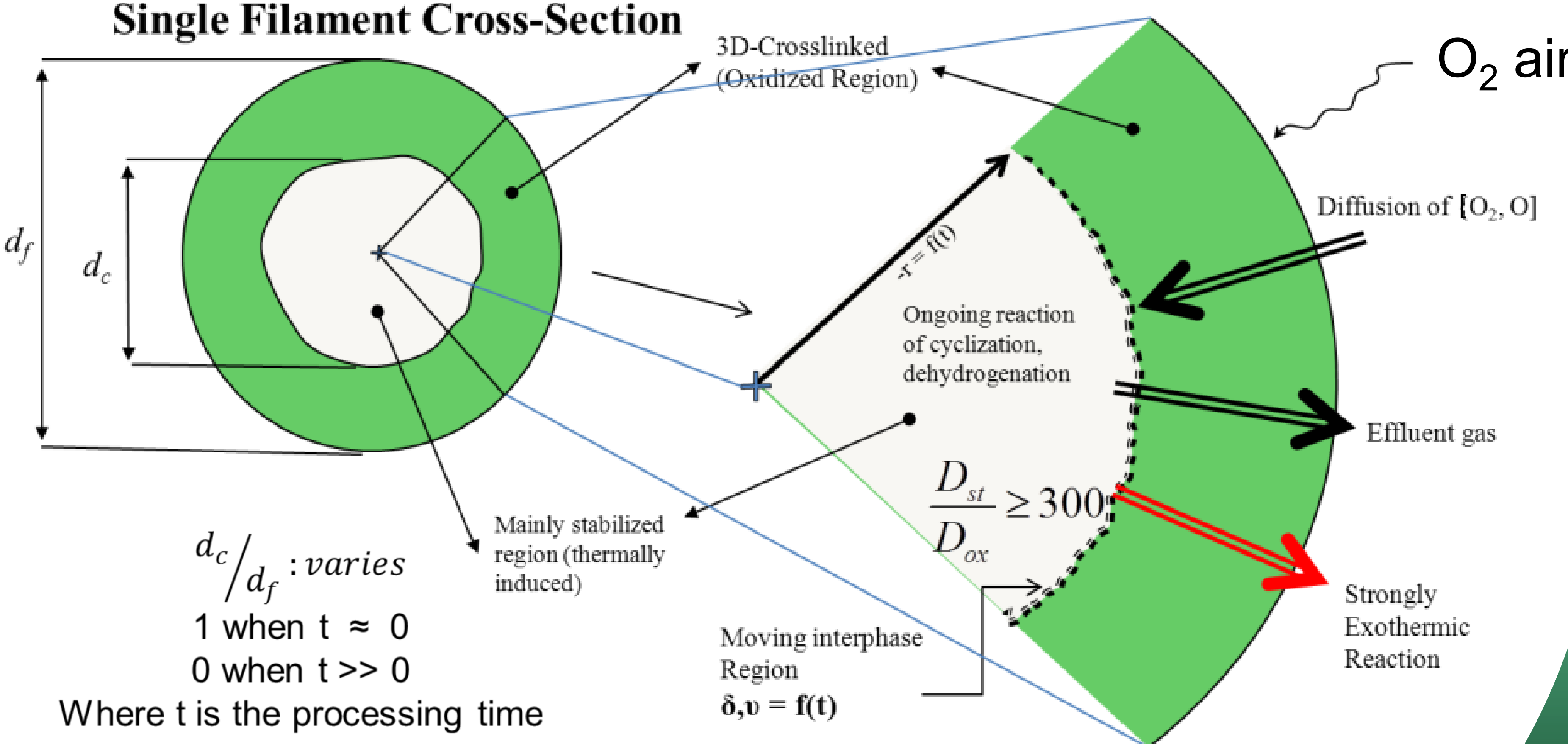
Tensile property requirements are 250 ksi, 25 Msi, 1% ultimate strain

ORNL is developing major technological breakthroughs for major cost elements

Approach: Reduce PAN-Oxidation

Two Zone Morphology

Single Filament Cross-Section



d_c/d_f : *varies*

1 when t ≈ 0

0 when t >> 0

Where t is the processing time

- **Diffusion of oxygen to reactive sites is restricted, sequent reactions follow more slowly**
- **The limiting factor in the oxidative processing is the diffusion-controlled phase**

Approach/Strategy
Plasma-Based Oxidation

- **Addresses diffusion-controlled stages of conventional oxidation.**
- **Utilization of non-thermal atmospheric pressure plasma processing versus more common thermal plasmas.**
- **Initially this technique was based on Remote Exposure (RE). The new method is now based on Close Proximity Indirect Exposure (CPIE).**
- **After carbonization – good physical, morphological, and mechanical properties.**
- **Residence time reduced by 2 - 3X (less than 35 minutes) when compared to conventional PAN oxidation.**
- **Small Reactor for parametric evaluations still in operation.**
- **Large Reactor under construction for Pilot-Scale testing.**
- **It is important to note that this project is no longer just a research and development effort – we are also now in a scale-up phase.**

Milestones

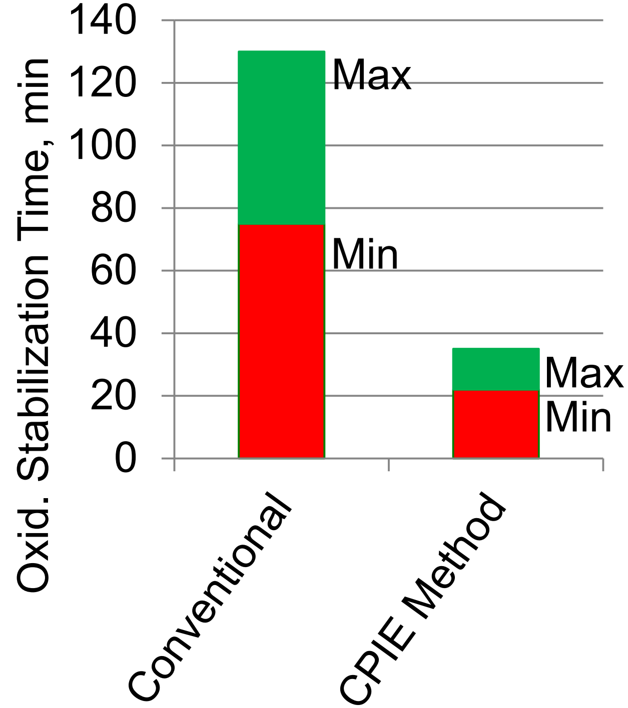
Date	Milestone	Status
January 2012	Plasma oxidize three 3K filament tows in less than 35 minutes that yields ≥250ksi tensile, ≥25 Msi Modulus.	**Complete**
October 2012 GO/NO GO	M1: Plasma oxidize one textile grade ≥20k tow at half of the conventionally required residence time that yields ≥250ksi tensile, ≥25 Msi Modulus.	**Complete**
January 2013	M2: Complete construction and installation of stretcher system as a component of the Large Reactor. Perform and report first test results of complete fiber handling subsystem within 15% of design parameters.	In progress
September 2013	M3: Establish definable relationships between tensile strength and modulus of oxidized fiber with primary advanced oxidation parameters.	In progress
September 2013	M4: Complete construction of all components for the Large Reactor for plasma oxidation. Verify proper operation of all subsystems.	In progress
March 2014 GO/NO GO	M5: Plasma Oxidize 3 tows of at least ≥20k in ≤35 min. that yields ≥250ksi tensile, ≥25 Msi Modulus. Variation in oxidized fiber mech. Prop. intow to tow ≤+-15%.	

Technical Accomplishments

Up to last MR2012 (Refresher)

- **CPIE technology was evaluated and implemented successfully.**
- **Plasma oxidation of three aerospace grade PAN tows (3k) was oxidized <35 min. Exceeded programmatic requirements.**
- **Focused then moved to large tows (24k) of low cost textile grade PAN. Required significant degree of parametric reevaluation.**
- **Large Reactor:**
  - **Design completed.**
  - **Construction of the main oven structure was begun and completed.**
  - **Structural components were delivered.**
  - **Assembly of all components and programming of the control and logging system, was begun.**

Technical Accomplishments FY13



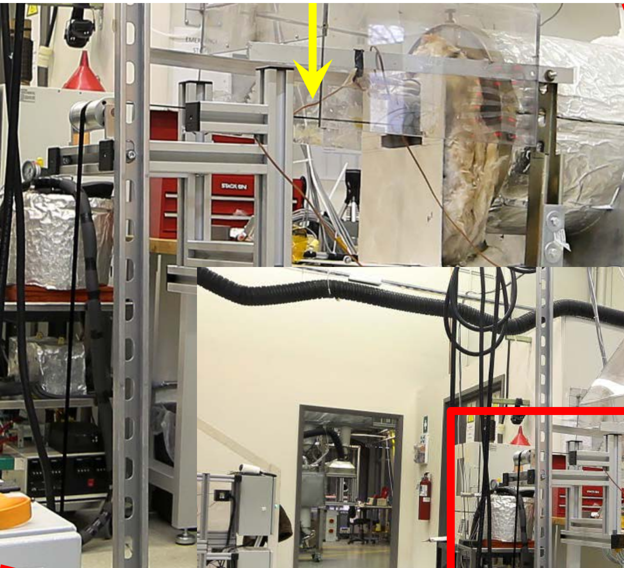
- Milestone M1 was met. A single 24k textile grade PAN tow was oxidized in less than 35 minutes while exceeding the program mechanical requirements.
- Assembly and programming of the Large Reactor is continuing and is projected to occur at the end of FY13. (FY14 will see shakedown testing and initial processing of fiber.)
  - Subsystems include the command and control, plasma generation, thermal control, flow control, exhaust treatment, and fiber handling equipment.
  - For meeting milestone M2, the stretching system is slated to be delivered at the end of March 2013.
- Data analysis of all textile grade PAN data has begun. The goal is to demonstrate controllability of the plasma oxidation process.
- A new patent was filed with the USPTO on November 19, 2012 covering the new CPIE technology.

Technical Accomplishments

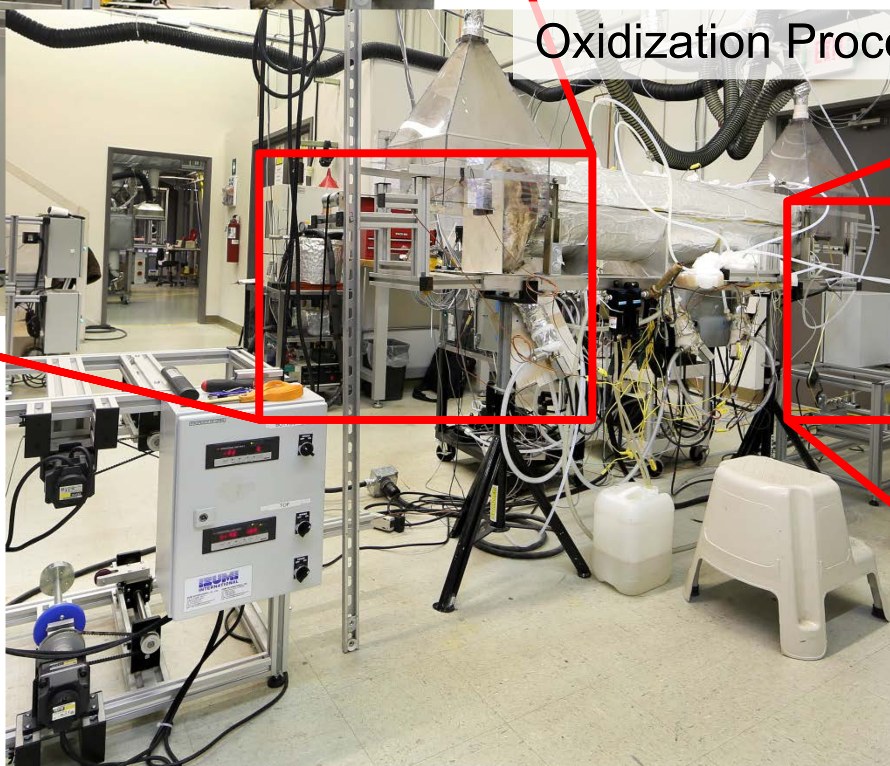
CPIE with the Small Reactor

Adapted for use with new CPIE plasma method. Designed for single tow processing only but was successfully used for three-tow processing. Used to validate CPIE and parametric studies/optimization of textile grade PAN fiber.

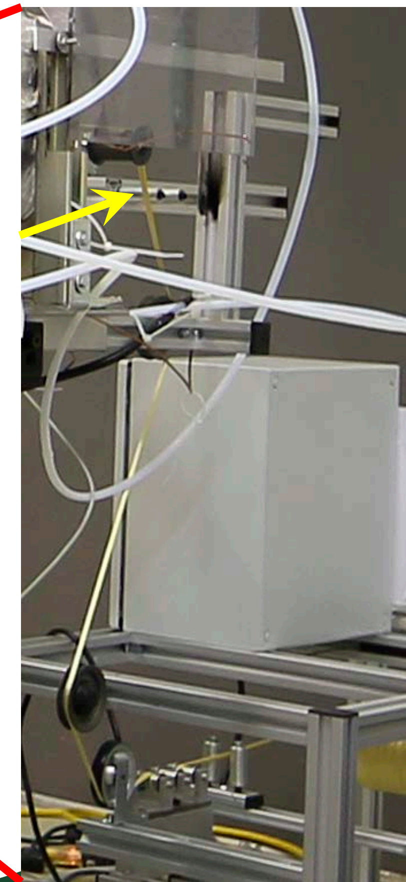
Textile Grade 24k
Oxidized PAN Fiber (OPF)



Oxidization Process



Textile Grade 24k
PAN Precursor



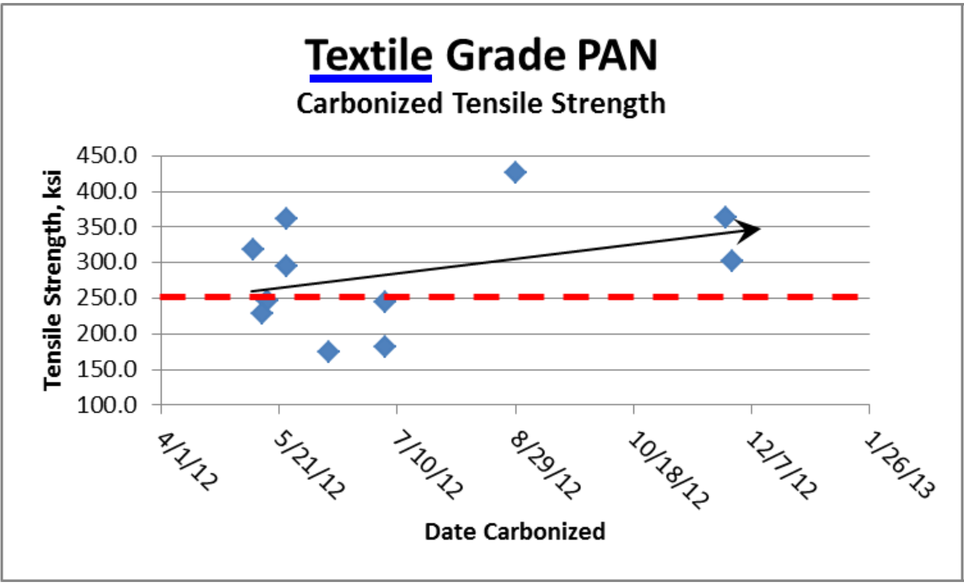
Technical Accomplishments

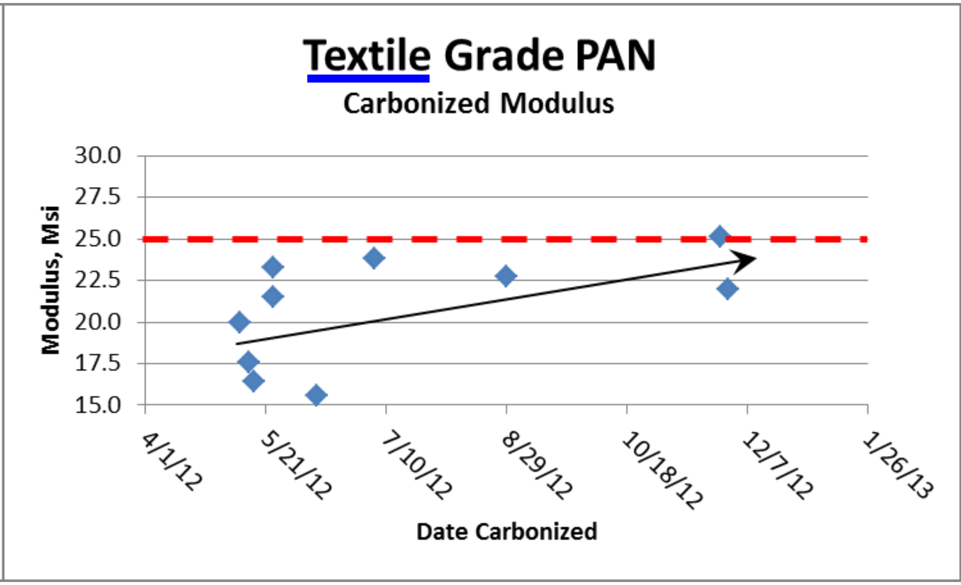
(Select Textile PAN 24k Fiber Mechanical Data – From Small Reactor)

Treatment		Oxidized				Carbonized			
Sample	Date Oxidized	Fiber Diameter (um)	Peak Stress (ksi)	Modulus (Msi)	Strain @ Break (%)	Fiber Diameter (um)	Peak Stress (ksi)	Modulus (Msi)	Strain @ Break (%)
Conventional	7/17/2008	12.9	60.1	0.9	11.72	6.36	409.1	25.5	1.48
SR589	4/25/2012	10.81	28.0	0.95	18.79	6.97	246.6	16.4	1.41
SR590	4/27/2012	11.85	21.7	0.77	18.00	6.81	228.0	17.6	1.19
SR591	4/27/2012	9.59	25.5	0.82	12.95	6.22	318.4	20.0	1.49
SR599	5/16/2012	9.93	24.3	1.03	10.05	N/M	N/M	N/M	N/M
SR600	5/22/2012	9.37	30.2	1.13	14.11	6.02	361.9	23.3	1.44
SR601	5/22/2012	9.69	31.3	0.97	25.74	6.29	294.6	21.5	1.30
SR604-2	6/5/2012	8.26	32.1	0.92	21.26	5.16	244.3	23.8	1.00
SR605	5/31/2012	8.53	27.7	0.89	15.82	6.74	174.5	15.6	1.08
SR610	6/7/2012	N/M	N/M	N/M	N/M	6.70	181.8	14.1	1.19
SR625	8/29/2012	8.53	28.1	0.92	19.19	5.4	425.2	22.7	1.8
SR638	11/26/2012	8.74	25.9	1	5.4	5.6	363.5	25.1	1.47
SR646	12/11/2012	N/M	N/M	N/M	N/M	5.72	302.2	22	1.2

Technical Accomplishments

(Select Textile PAN 24k Fiber Mechanical Data – From Small Reactor)





These results reflect two issues:

1. Textile grade chemistry is more of a challenge to deal with.
2. The Small Reactor has only one single thermal zone for the entire oxidation stage.

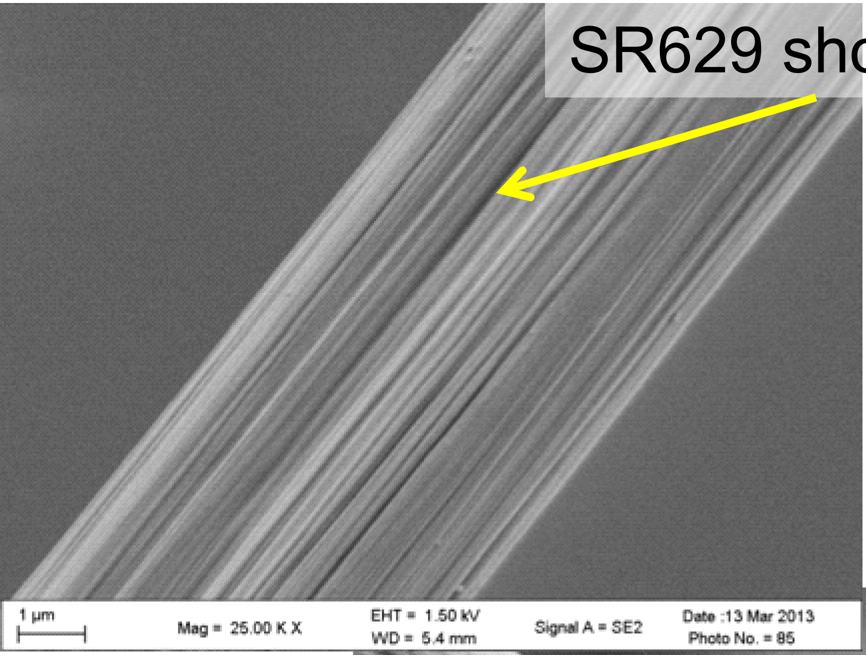
Through modification of the typical process, the research team was able to introduce a thermal gradient along the length of the reactor to alleviate this problem. The design of the Large Reactor eliminates this issue.

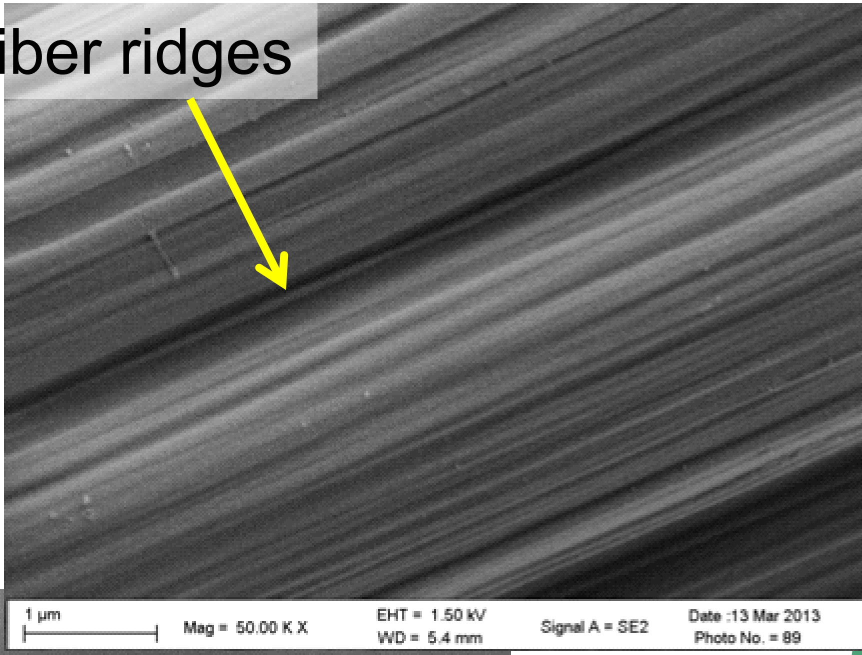
Dashed red line denotes program requirements.

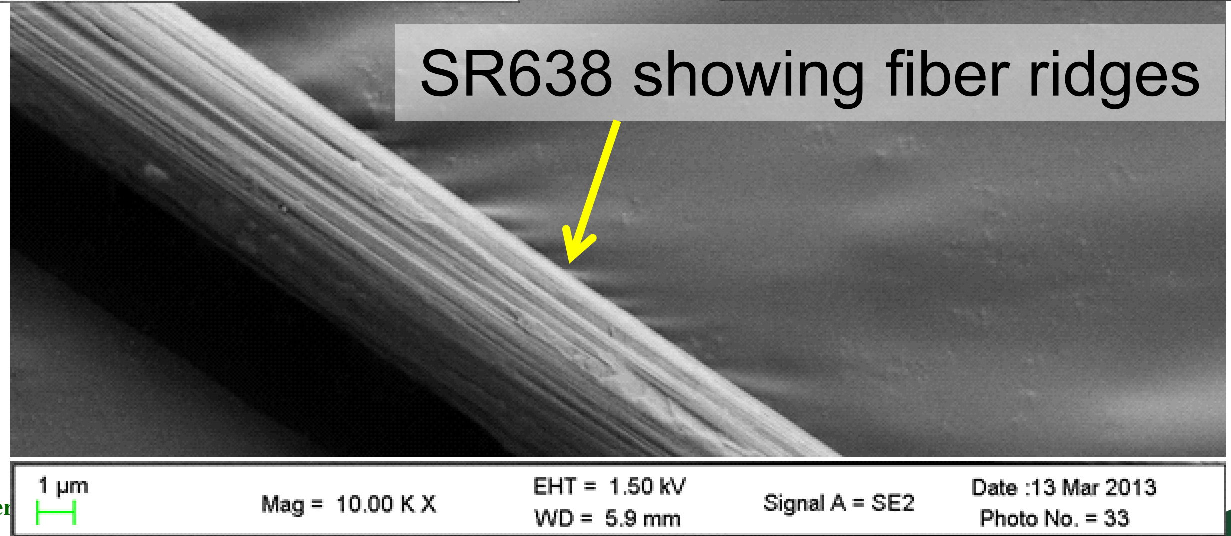
Technical Accomplishments

(Textile PAN 24k Fiber – From Small Reactor) Plasma Oxidized, Conventionally Carbonized

SR629 showing fiber ridges

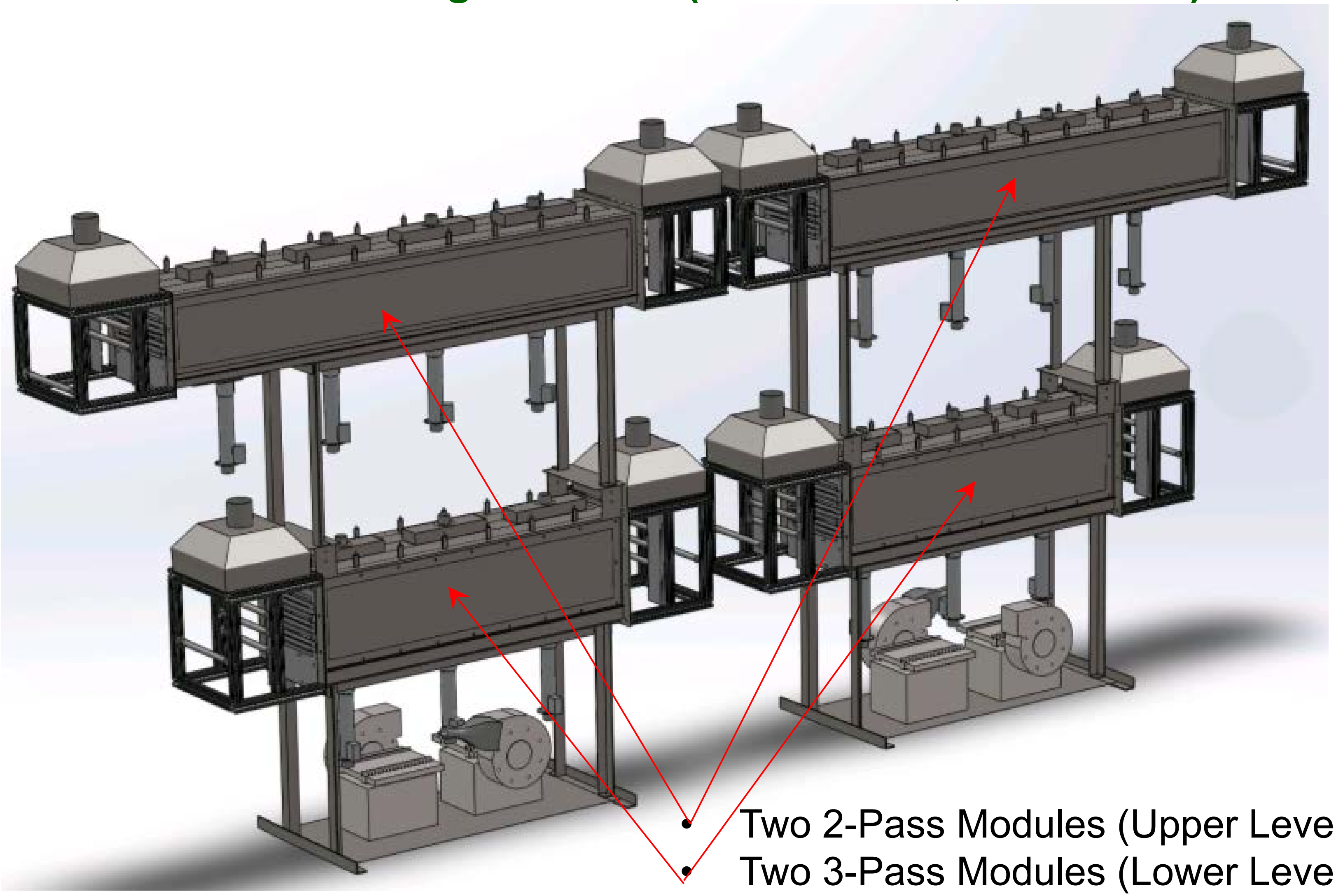






Technical Accomplishments

Large Reactor (as delivered, June 2012)



- Two 2-Pass Modules (Upper Level)
- Two 3-Pass Modules (Lower Level)

Technical Accomplishments

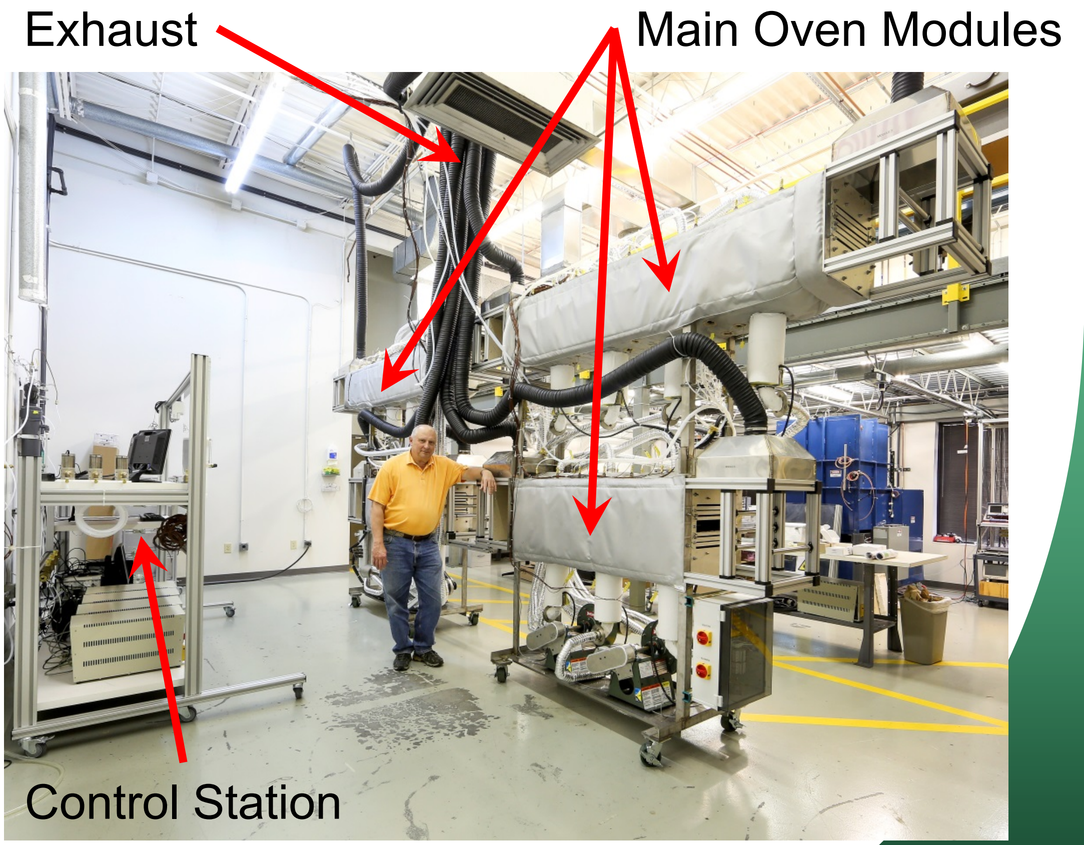
Large Reactor (as of February 2013)

The Large Reactor:

- At the Pilot-Line level, designed with a plate capacity circa 1 ton/year.
- If successful, can be directly integrated into the small ORNL Carbon Fiber Conversion Pilot Line.

Specifications:

- 4 independently controlled thermal zones
- Multiple passes in each zone
- Fiber movement system designed for a max of 6 large tows (not shown).
- Highly modular and flexible
- Utilizes CPIE technology (plasma hardware not shown)
- LabVIEW controlled



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Collaboration and Coordination

- **Extensive contact with leading R&D people/institutions in this matter (*under limitations of IP and export control*).**
- **The technical progress achieved on this project is the result of very close and effective collaboration between ORNL and RMX.**
- **Interest in utilizing this technology has been expressed repeatedly by many parties. Three companies including CF equipment manufacturers and CF producers.**
- **Representatives of three companies have visited the research team's facilities both at ORNL and RMX. Both have requested continued updates of this development effort.**

Future Work

- **Rest of FY13**
  - Complete construction of Large Reactor
  - Complete data analysis of textile PAN plasma oxidation in Small Reactor
  - Continue interactions with interested companies
- **FY14**
  - Verify continuous operation capabilities of Large Reactor
  - Process multiple tows of large textile grade PAN with low variability among tows
  - Obtain scaled energy consumption data
- **FY15**
  - Deliver, install, and commence operations of plasma oxidation reactor in the ORNL Small Pilot Line (SPL). Evaluation needed both as standalone unit, and incorporated inline with ORNL SPL.
  - Deliver equipment specification for a plasma oxidation module for an advanced technology/demonstration pilot line (principal project deliverable) appropriate for integration with the Carbon Fiber Technology Facility.

Conclusions

- This has been a very successful project year
- CPIE technology was demonstrated to be successful with textile grade large tow PAN precursor (24k).
- This technology is on track to be scaled up. The Large Reactor, currently being assembled, will provide one large step towards this goal.
- The ultimate goal of this project is to successfully demonstrate this technology at a sufficiently large scale such that the carbon fiber industry *begins widespread utilization of this technology.*

Summary

Relevance

- This technology will reduce the required oxidation time during conversion, and hence will reduce the production costs of carbon fiber.

Approach/Strategy

- Develop an oxidation technology that addresses the diffusion time limitations of the conventional method and scale that technology sufficiently to demonstrate the success of this approach to the carbon fiber industry.

Technical Accomplishments

- CPIE method validated and patent filed
- Large tow textile fiber were successfully processed.
- Large Reactor assembly continues.

Collaboration and Coordination

- ORNL and RMX are partners.
- Pursuing interested parties. Continuing communications.

Future Work

- Complete Large Reactor and begin operations.
- Demonstrate large scale CPIE technology.

Thank you for your attention.

"Troupial" (*Icterus icterus*)

Questions?

Technical Backup Slides

Chronological Textile PAN Progress

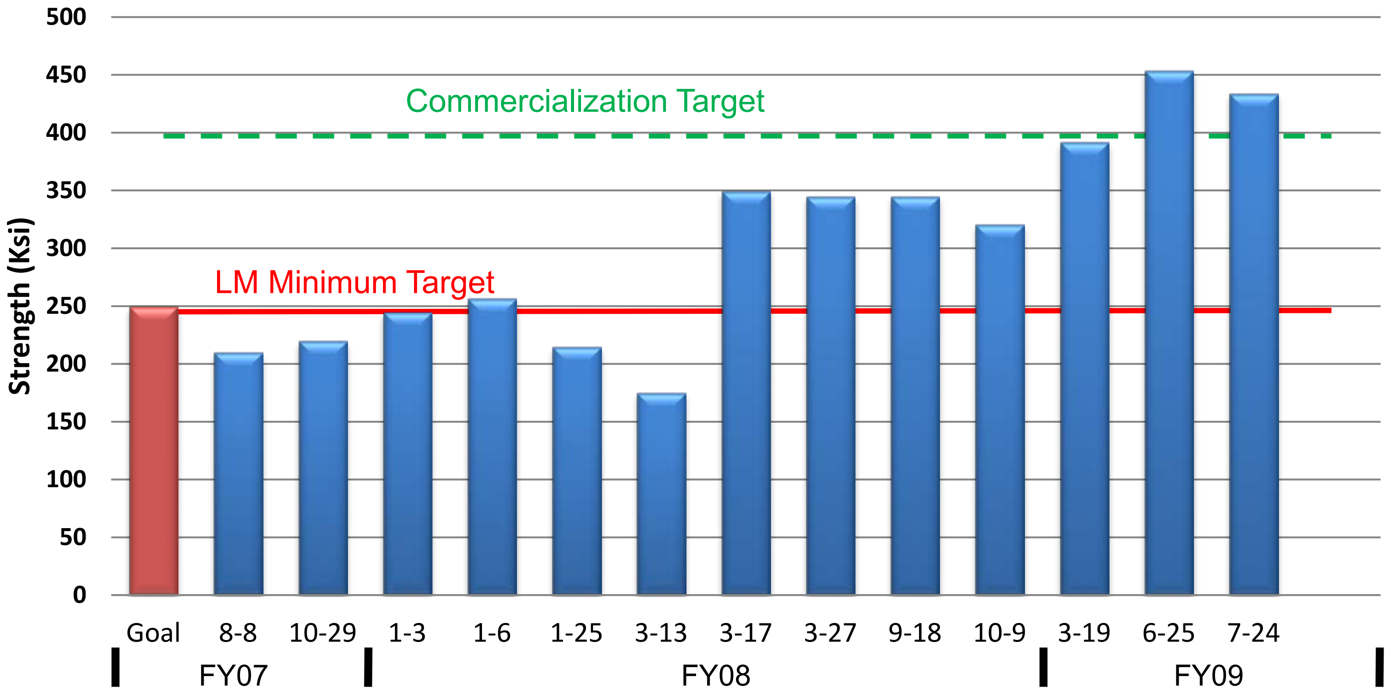
LM006

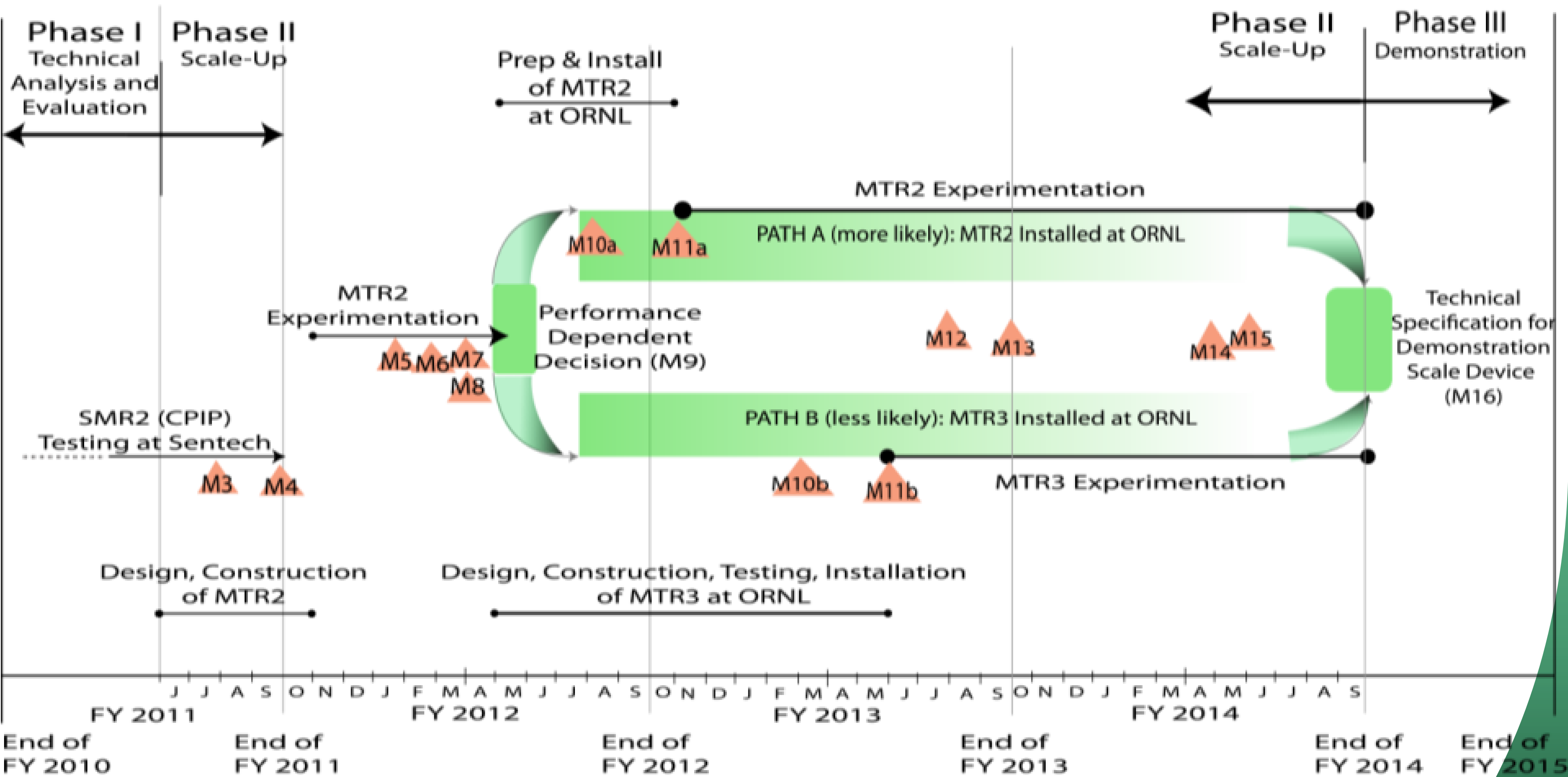
Conventional Conversion/Analysis of two PAN Precursors

As a reference, it took over two years to find the proper conversion conditions for the textile precursor. For the aerospace fiber, this time was reduced significantly (~3 months).

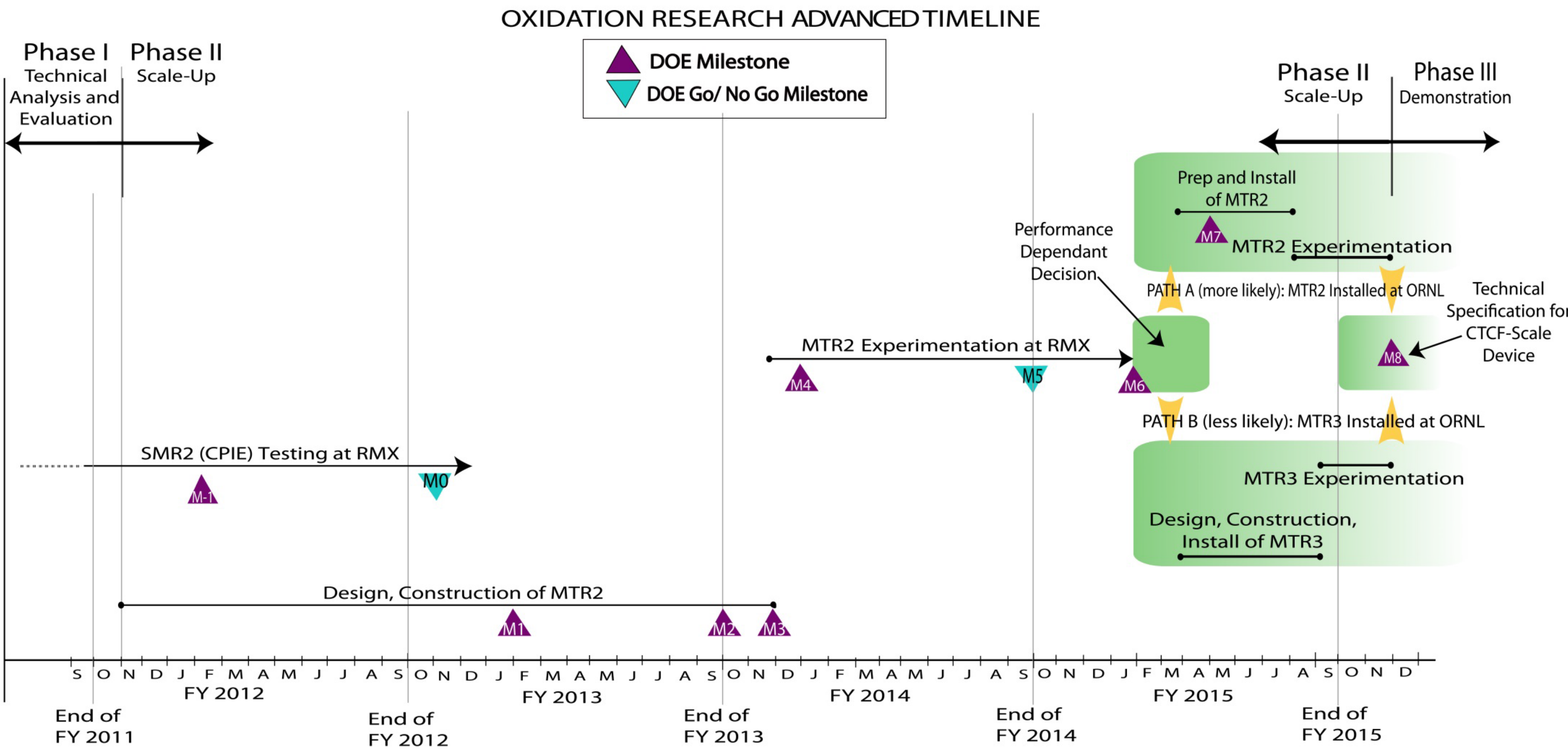
Target Properties:
Strength: 1.72 GPA (250 KSI)

Current Properties:
Strength: 3.13 GPA (454 KSI)





$2M Yearly Budget



$1M Yearly Budget